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SCIENTIFIC DATA REVIEWS
EPA SERIES 361

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

September 28, 2001

MEMORANDUM

SUBJECT: EPA Review of "Dissipation of Dislodgeable Residues of 3336 WP from Cut Flowers (MRID No. 450275-01), PC Code # 102001, DP Barcode D263201.

FROM: Gary Bangs
Reregistration Branch 3
Health Effects Division (7509C)

TO: Deanna Scher, Chemical Review Manager
Special Review and Registration Division (7508C)

THROUGH: Cathy Eiden, Branch Senior Scientist
Reregistration Branch 3
Health Effects Division (7509C)

This study met most of the requirements in OPPTS Series 875 of the Occupational and Residential Exposure Test Guidelines (U.S. EPA 1997) and can be useful in determining exposures to thiophanate-methyl residues on roses, carnations, and other plants in a greenhouse setting. The dislodgeable foliar residue (DFR) values for roses and mums are sufficiently similar to be combined and used to predict worker exposure when adjusted for application rate. Residues of the breakdown product, MBC, were low but followed no predictable pattern.

EXECUTIVE SUMMARY

The registrant submitted a study in February, 2000 to determine dislodgeable foliar residues (DFR) on cut flowers. The study, which was conducted on roses and mums in greenhouses, appears to meet most of the OPPTS Series 871 Post-Application Exposure study guidelines. The study was conducted in only one geographic location in two greenhouses, but geography has little effect on the actual greenhouse environments. The 3336 WP label recommends that 24 oz product/100 gal water be used, and multiple applications 7-10 days apart with no maximum number of applications specified. The study flowers were sprayed using a high-pressure handgun with 16 oz of 3336 WP (50% thiophanate-methyl in water-soluble bags) per 100 gallons of water, which is only two-thirds of the label maximum rate. Two applications were made, seven days apart, at an actual rate of 1.05-1.18 lb ai/acre. Residues were collected and dislodged in compliance with OPPTS Guidelines. Average field fortification recovery values ($108 \pm 8.3\%$) exceeded the guideline standard, therefore the residue data did not require correction.

The measured DFRs of thiophanate-methyl increased from zero to one days-after-treatment (DAT 0-1), remained constant through DAT 5, and declined slowly after DAT 7. The dissipation rate was calculated using the DFR data after the second application, using semi-log regression of the thiophanate-methyl and MBC residues for each site separately. The thiophanate-methyl residue dissipation half-lives were calculated at 11.8 days for roses ($R^2=0.85$), and 19.0 days for mums ($R^2=0.91$). As the table below shows, predicted residues remain well above the level of quantification ($0.0125 \mu\text{g}/\text{cm}^2$) 90 days after application. The data were combined and the semi-log regression showed sufficient correlation (R^2 of 0.97) that these values (adjusted for application rate) may be used to estimate worker greenhouse exposure.

The thiophanate-methyl degrades to another pesticide MBC, which has different toxic effects of concern. MBC residues, though low, were well above LOQ for many weeks after application, and were higher on mums than on roses. The MBC residues slowly rose to a maximum 2 and 3 weeks after application for mums and roses, respectively. These data do not fit a first order dissipation pattern, and so semi-log linear regression equations yield predicted values with poor correlation ($R^2 < 0.5$) to the log-transformed data. The maximum mean DFR value for MBC was $0.35 \mu\text{g}/\text{cm}^2$ on DAT 14 for the mums.

Thiophanate-methyl: [MRID 45027500]; Avg DFR [Rose & Mum], 19-day Half-Life	
DAT	Average Study Residue [DFR $\mu\text{g}/\text{cm}^2$]
0	5.000
1	4.813
2	4.632
3	4.458
4	4.291
5	4.130
6	3.975
7	3.826
14	2.928
21	2.241
28	1.715
35	1.312
42	1.004
43	0.966
44	0.930
49	0.768
56	0.588
63	0.450
70	0.344
77	0.264
84	0.202
89	0.167
90	0.160

Values calculated on spreadsheet and results rounded to two significant figures. Workers wearing long pants, long sleeved shirts and no gloves.

DAT = Days after treatment with thiophanate-methyl.

DFR = Best-fit predicted thiophanate-methyl dislodgeable foliar residue from study; linear regression of raw data after correcting for field fortification recovery.

ATTACHMENT

Forrest, D. Review of *Dissipation of Dislodgeable Residues of 3336 WP from Cut Flowers* (MRID No. 450275-01). Versar, Inc. March 6, 2000.



MEMORANDUM

TO: Gary Bangs cc: 3772.101
J. Becker

FROM: Diane Forrest

DATE: March 6, 2000

SUBJECT: Review of *Dissipation of Dislodgeable Residues of 3336 WP from Cut Flowers*
(MRID No. 450275-01)

This report reviews *Dissipation of Dislodgeable Residues of 3336 WP from Cut Flowers*, submitted by Elf Atochem North America, Inc. in support of reregistration requirements for the fungicide thiophanate-methyl. The requirements for this study are specified by the U.S. Environmental Protection Agency's (US-EPA) OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar Residue Dissipation: Agricultural. The following information may be used to identify the study:

Title:	<i>Dissipation of Dislodgeable Residues of 3336 WP from Cut Flowers</i> , 160 pages
Sponsor:	Luis Castro Elf Atochem North America, Inc. 200 Market Street, 21st Floor Philadelphia, PA 19103-3222
Field Study Test Sites:	Lainie Petrie Grayson Research, LLC. 1040 Grayson Farm Road Creedmoor, NC 27522
Analytical Laboratory:	Elf Atochem North America, Inc. 900 First Avenue King of Prussia, PA 19406
Study Director & Author:	Stephen A. Ampofo Elf Atochem North America
Report Date:	January 7, 2000
Identifying Codes:	MRID # 450275-01, Sponsor Study No. KP-98-47

Executive Summary

This report reviews a dislodgeable foliar residues (DFR) study submitted by Elf Atochem North America, Inc. in support of reregistration requirements for the fungicide thiophanate-methyl, the active ingredient in 3336® WP. This product, a wettable powder formulation packaged in water-soluble bags, contains 50 percent thiophanate methyl. Mature roses and chrysanthemums grown in a greenhouse were treated twice (7 days apart), and DFR samples were collected up to 84 days after treatment. DFR samples were analyzed for thiophanate methyl and methyl-2-benzimidazole carbamate (MBC), a breakdown product.

Elf Atochem calculated dissipation half-lives for thiophanate methyl (TM), by running a linear regression of the natural logarithms of uncorrected, average DFR values at certain specific time-points. For TM residues on roses, the authors used DAT-1, 3, 5, 7, 14, and 21 data after the first application only. For TM residues on mums, the authors used DAT-0, 1, 3, 5, and 7 data after the first application only. This resulted in calculated thiophanate -methyl dissipation half-lives of 18.2 days on roses ($R^2 = 0.95$), and 18.7 days on mums ($R^2 = 0.91$). Dissipation half-lives for MBC were not calculated, since the magnitude of the MBC values was judged to be too low.

Versar re-ran the dissipation kinetics analysis using all individual TM data points (not averages) for DAT-0 through DAT-84 for both thiophanate methyl and MBC after the second application. In accordance with EPA guidance, Versar assumed first order dissipation kinetics prevailed. Versar then applied Microsoft EXCEL®'s 7.0 linear regression function to uncorrected, log (ln) transformed data. Versar calculated TM dissipation half-lives of 11.8 days on roses ($R^2 = 0.85$), and 19.0 days on mums ($R^2 = 0.91$).

Versar found that MBC residues, though low, were well above LOQ for many weeks after application, and were higher on mums than on roses. A linear regression run on the MBC DFR data-set yielded a dissipation half-life of 44 days ($R^2 = 0.53$) on mums, and for roses, the dissipation half-life was 51 days ($R^2 = 0.20$). These data do not seem to fit a first-order dissipation model.

Versar found the study to be generally well-written and well-organized. It met OPPTS Group B guidelines in most significant respects. The most important discrepancies and issues of concern were the following:

- In this study, the application rate was lower than the maximum allowable (16 oz/100 gallons applied rather than 24 oz/100 gallons specified on the product label), and there were only two applications at an interval of seven days. The 3336WP label-specified application interval is 7-10 days, with no maximum number of applications.

- The product label recommends use of a wetting agent “for plants that have leaves that are difficult to wet properly,” and “use of a spreader/sticker to enhance product performance in wet weather conditions.” Information in Appendix C, page 102-3 of the Study Report, seems to indicate that surfactants were not added to the tank mixes.
- No tank mix samples were analyzed and no deposition plates were analyzed. These data might have provided information to verify field application rates.
- Fortified field recovery values were satisfactory. However, Versar noted that about one-third of the thiophanate methyl rose DFR and two-thirds of the mum DFR field sample data-points (i.e. 13/36 - roses and 24/36 - mums) were higher than the highest fortification level. All of the MBC field DFR sample data were below the lowest fortification level, which was 200 $\mu\text{g}/\text{sample}$. [Specifically, all rose DFR data were less than 100 $\mu\text{g}/\text{sample}$, and all mum DFR data were less than 170 $\mu\text{g}/\text{sample}$.] The study quality would have been improved if the field fortification levels chosen were more reflective of the sample results obtained.
- A total of 56 field fortified control samples were prepared (i.e., 28 each for roses and mums). However, not all of these were analyzed (see page 116 of the Study Report). Only 14 samples were analyzed for roses, and 14 for mums. Also, except for the pre-application #1 samples, single replicates at 200 $\mu\text{g}/\text{sample}$ and 1,000 $\mu\text{g}/\text{sample}$ fortification levels were analyzed from DAT-0 onwards. The authors do not explain whether the samples that were analyzed were randomly selected, nor what became of the rest of the samples.
- The authors did not report dates of individual sample analyses. The authors stated that “the longest creation-to-analysis interval for a field sample was 146 days whereas the longest such interval for a field spike was 158 days.” The field spike analyzed on the 158th day seems to have been a single, 200 $\mu\text{g}/\text{sample}$ spike which had originally been analyzed on the 112th day. It seems to have been reanalyzed on the 158th day. It appears that all other field spike samples may have been analyzed after much shorter storage times than the oldest field sample.

STUDY REVIEW

Study Background

This report reviews a dislodgeable foliar residues (DFR) study submitted by Elf Atochem North America, Inc. in support of reregistration requirements for the fungicide thiophanate-methyl. Elf Atochem conducted the study in response to: 1) a March 1, 1993 Data Call-In (DCI) notice for data necessary to calculate transfer coefficients, and 2) an October 18, 1995 DCI. Thiophanate methyl is the active ingredient found in 3336® WP, the product applied in this study. "3336® WP" is a wettable powder formulation, packaged in water-soluble bags, which contains 50 percent thiophanate methyl (i.e. dimethyl 4,4-o-phenylenebis-(3,thioallophanate); CAS No. 23564-05-8).

Field-phase work was conducted by Grayson Research, LLC at two commercial quonset greenhouses operated at the Grayson Research facility, located near Creedmoor, North Carolina. Mature roses and chrysanthemums were treated twice (7 days apart) with 3336® WP, and samples were collected between April 22 and July 22, 1999. All samples were analyzed by Elf Atochem North America, in King of Prussia, PA. Sample analyses were conducted between August 12, 1999 and September 29, 1999.

Test Sites

One greenhouse was set aside for collection of untreated control DFR samples. The other "treated" greenhouse was located 24 feet away. The authors state: "A rose variety commonly used for greenhouse culture, cultivar *Double Delight* hybrid tea, was assigned Plant A, and a chrysanthemum variety, cultivar *Vero*, was designated Plant B in the trial. Typical cultural practices were used to grow the cut flower crops."

The authors stated: "Each greenhouse consisted of a tubular frame, double-poly covered structure with polycarbonate end walls. Each greenhouse [was] 48 feet long and 28 feet wide. The floor of each greenhouse consisted of black landscape fabric over porous base material." Greenhouses were cleaned with a bleach solution prior to setup.

Roses were shipped to the test site as bare-root plants on January 22, 1999. They were planted and grown at ambient temperatures ranging between 68° F. and 78° F. On April 9, 1999, roses were arranged into three 40-foot rows in the treated greenhouse, and one 40-foot row in the untreated greenhouse. Roses were watered by injector daily.

Chrysanthemums (mums) were planted as cuttings on January 14, 1999 and grown at ambient temperatures ranging between 62°F. and 78 ° F. On April 12, 1999, the mums were arranged in double 40-foot rows in the treated greenhouse, and double 32-foot rows in the untreated greenhouse. Mums were watered by injector daily.

Maintenance and Pesticide Use History

Cultural practices and maintenance compounds used are listed in Tables II and III on page 85 of the Study Report. Roses were treated three times with Rose Guard® (a.i. disulfoton and trifluralin) and twice with Orthene® (a.i. acephate). Chrysanthemums were treated once with Osmocote (a.i. unknown) and three times with Orthene® (a.i. acephate). Some of these applications were made after the test compound was applied.

Table 1. Pesticide Use History

Date Applied	Chemical Applied	Cut Flower Crop Treated
1/14/99	Osmocote	Mum
2/16/99	Rose Guard®	Rose
3/25- 3/26/99	Rose Guard®	Rose
4/19/99	Orthene®	Mum
4/22/99	Thiophanate Methyl	Rose/Mum
4/22/99	Thiophanate Methyl	Rose/Mum
4/29/99	Thiophanate Methyl	Rose/Mum
4/29/99	Thiophanate Methyl	Rose/Mum
5/13/99	Orthene®	Mum
6/4/99	Rose Guard®	Rose
	Orthene®	Mum
6/11/99	Orthene®	Rose
6/18/99	Orthene®	Rose

Greenhouse Environmental Conditions

The authors stated: "Each greenhouse was equipped with a 42-inch CoolAir exhaust fan, a 3 by 15 foot Carolina Cooler evaporative cooler, a 175,000 BTU Modine propane fired heater, two 20-inch Uniflow horizontal airflow fans, and a 36-inch Jaderloon motorized intake shutter.

An irrigation system provided water to both greenhouses. Environmental control and monitoring was provided by a Q-Com GEM III computer system.”

The authors stated: “...During the applications, all fans, evaporative cooling pumps and heaters were turned off in both the treated and the untreated greenhouses.”

Table VI on page 87 of the Study Report summarizes average daily maximum and minimum temperature and humidity (as single values for each parameter) over the application and sampling period (April 22 to July 22, 1999). In the treated greenhouse, the average daily temperature ranged from 65.9° F. to 79.7° F., and humidity ranged from 69.1 to 93.9 percent. However, no information about the variability of these values over this rather long period was reported.

Materials and Equipment

Elf Atochem provided a 3336® WP product label for review. “3336® WP” is a wettable powder formulation, packaged in water-soluble bags, which contains 50 percent thiophanate methyl. According to the product label, the maximum application rate for horticultural applications is 24 oz formulated product per 100 gallons against powdery mildew, which is a disease of roses and mums. [However, 16 oz formulated product/100 gallons is the maximum rate for blackspot of roses.] Multiple applications may be made at 7-10 day intervals, or as specified against a particular pest.

In this study, the application rate used (i.e. 16 oz formulated product/100 gallons) was lower than the maximum allowable. A 10-gallon tank mixture was prepared for the first application and a 7.64 gallon tank mix was prepared for the second application. Page 86 notes that between 2 and 3 gallons of the spray mix were applied to the test plots per application (e.g. between 209 and 235 gallons per Acre spray solution or between 1.05 and 1.18 lbs ai/A applied, see page 80). Plants were sprayed “to drip,” and “targeted complete coverage of the cut flower plants without excess runoff.” Only two applications were made, at an interval of seven days.

Appendix C, page 101 of the Study Report, details sprayer calibration and application rate calculations. Applications were made using a tractor-mounted cone tank sprayer with a power take-off diaphragm pump, equipped with a handgun sprayer and fitted with a D4 weed systems disc nozzle. One spray pass was made on each side of the treated replicates, using an upward and downward motion.

The label also recommends use of a wetting agent (“such as Clearly’s SUPER WET”) “for plants that have leaves that are difficult to wet properly. Use of a spreader/sticker such as Cleary’s CLEARSPRAY T/O is recommended to enhance product performance in wet weather conditions.” Information in Appendix C, page 102-3 of the Study Report, seems to indicate that neither surfactants nor spreader/stickers were added to the tank mixes.

Sampling of Dislodgeable Foliar Residues

DFR samples were collected from roses and mums at the following intervals: before the first application and at days 1, 3, and 5 after application #1. Samples were also collected before the second application, and at DAT-1, 3, 5, 7, 14, 21, 28, 42, 56, 70, and 84. Triplicate samples were collected at each sampling interval.

Leaf disc samples were collected with a 2.54 cm diameter Birkestrand leaf punch. Forty samples were collected per sample, into a Teflon-capped amber glass jar. The jars were stored on Blue Ice in coolers in the field. Samples were dislodged at the field laboratory within 5 hours of collection in a freshly prepared 0.01% v/v Aerosol OT® solution. Samples were shaken on a reciprocating shaker (~200 cycles/minute) for 10 minutes. Solutions were decanted into jars containing 100-200 mg of L-cysteine. The extraction was repeated and both extracts combined.

QA/QC

Sample History

Table 1, page 18 of the Study Report, notes many significant field dates, such as planting dates, application dates, sampling dates, sample shipping dates, and the dates samples were received. However, dates on which specific field DFR samples were analyzed are not reported in the analytical report, nor are storage intervals given. The authors state on page 12 of the Study Report that sample analyses were conducted between August 12, 1999 and September 29, 1999. If the earliest sample collected had been analyzed last, the longest sample storage interval would then be 160 days. The authors stated that “the longest creation-to-analysis interval for a field sample was 146 days whereas the longest such interval for a field spike was 158 days.” [However, see page 9, below, referencing another statement that field fortified samples were stored between 33 and 141 days.]

Tank Mix Analyses

None were collected or analyzed.

Deposition Plates

Deposition plate samples were not prepared.

Analytical Methodology

A copy of the analytical methodology used was included for review (see page 65 of the Study Report), and the method was also described in the analytical report. The method is titled

“HPLC Analytical Method For the Simultaneous Determination of Thiophanate-methyl (TM) and Methyl-2-benzimidazole Carbamate (MBC) in Detergent Solution: Elf Atochem Method No. KP-016-02,” June 22, 1998. The proprietary method consists of filtering the detergent dislodging solutions, and directly injecting a 2 ml aliquot on an HPLC. A 40:60 mobile phase (i.e. methanol vs. 25 mM $(\text{NH}_4)_2\text{HPO}_4$ at pH 6.5). Programmable wavelength detectors were used to take advantage of absorption maxima for TM (~265 nm) and MBC (~285 nm).

Retention times were between 14.1 and 15 minutes for thiophanate methyl, and between 8.0 and 8.4 minutes for MBC.

Limits of Detection (LOD) & Limit of Quantitation (LOQ)

An LOD was not defined in this report. The method LOQ was reported to be 0.05 ppm for both thiophanate methyl and MBC. The analytical report identifies the LOQ as 10 $\mu\text{g}/\text{sample}$ or 0.0125 $\mu\text{g}/\text{cm}^2$.

Laboratory Recovery

Laboratory fortification samples were analyzed concurrently with each set of samples. Dislodging solutions were fortified at levels ranging from 50 nanograms/sample to 10 $\mu\text{g}/\text{sample}$ (i.e., 0.0013 $\mu\text{g}/\text{cm}^2$ to 0.25 $\mu\text{g}/\text{cm}^2$). The latter value was about 50 percent of the maximum field sample levels of thiophanate methyl found on mum leaves. The overall average recovery for thiophanate methyl was 114 ± 14.8 percent ($n=19$) and for MBC 114 ± 11.4 percent ($n=18$). Individual recovery values were satisfactory at all laboratory recovery fortification levels. See page 21 of the Study Report, for further detail.

Field Fortification Recovery

Field fortified samples were prepared on the day of each application (i.e., twice), and on DAT-14, 28 and 84 after the second application. Six replicates were prepared each time, except that only four replicates were prepared at DAT-28. Samples were dislodged and treated just as the field DFR samples. Samples were fortified at two levels ($N=3$): 200 μg TM and 200 μg MBC per sample for the “low” fortification and 1,000 μg of TM and 1,000 of MBC sample for the “high” fortification level. These levels were 20 and 200 times the LOQ, respectively.

It is noteworthy that about one-third of the thiophanate methyl rose DFR and two-thirds of the mum DFR field sample data-points fell outside this range (i.e. 13/36 - roses and 24/36 - mums). [All of the MBC field DFR sample data for roses were below 100 $\mu\text{g}/\text{sample}$, and all DFR field data were less than 170 $\mu\text{g}/\text{sample}$ for mums.] The study quality would have been improved if at least one additional fortification level had been included.

Although a total of 56 field fortified control samples were prepared (i.e., 28 each for roses and mums), not all of these were analyzed (see page 116 of the Study Report). Only 14 samples

were analyzed for roses, and 14 for mums. Except for the pre-application samples, where triplicate samples were analyzed at each fortification level, only single replicates at either the 200 $\mu\text{g}/\text{sample}$ or the 1,000 $\mu\text{g}/\text{sample}$ fortification level were analyzed from DAT-0 onwards. [The authors do not explain whether the samples that were analyzed were randomly selected, nor what was done with the rest of the samples.]

The overall field fortified recovery ranged between 84 percent and 118 percent (N=28) for thiophanate methyl and between 75 percent and 129 percent for MBC. The average overall recovery values were 108 ± 8.3 percent for thiophanate methyl and 110 ± 10.8 percent for MBC. Considered separately, the average field fortified recovery at 200 $\mu\text{g}/\text{sample}$ was 110.5 ± 10.5 percent (N=14), and 102.6 ± 7.8 percent at 1,000 $\mu\text{g}/\text{sample}$ (N=14).

Field fortified samples were stored between 33 and 141 days, according to a table on page 116 of the Study Report.

Storage Stability Recovery

No designated storage stability samples were analyzed for recovery. The authors relied on fortified field recovery samples as storage stability controls. The authors stated that “the longest creation-to-analysis interval for a field sample was 146 days whereas the longest such interval for a field spike was 158 days.” The field spike analyzed on the 158th day seems to have been a single, 200 $\mu\text{g}/\text{sample}$ spike which had originally been analyzed on the 112th day. It seems to have been reanalyzed on the 158th day. Otherwise, all other field spike samples were analyzed after much shorter storage times than the oldest field sample. (See page 116 of the Study Report).

Dates of analysis were not reported for individual field DFR samples, and individual sample storage intervals were not provided. Dates of analysis were reported for fortified recovery samples (although storage intervals were reported for these samples).

Results

Thiophanate methyl (TM) and MBC DFR values measured for roses were markedly lower than those measured on mums. The maximum TM DFR value for roses was 1,830 $\mu\text{g}/\text{sample}$, measured at DAT-1. The maximum TM DFR value for mums was 2,510 $\mu\text{g}/\text{sample}$, measured on DAT-0. Thiophanate methyl DFR values for roses may have dropped to near LOQ by DAT-84 (note that only two of three replicates did so), however TM DFR values on mums were still well above LOQ by DAT-84.

A high percentage of sample data exceeded the highest field fortification control level used in this study (i.e., 1,000 $\mu\text{g}/\text{sample}$ -see Table 3, below, for a breakdown). Therefore, the field fortification levels were not well matched to the data set. Nevertheless, the average field

fortified recovery values for both TM and MBC exceeded the guideline value (i.e. >90 percent and <110 percent). See Table 2, below.

Table 2 - Summary of Thiophanate-Methyl Turf-Transferrable Residue Data

Study Sample Set	Maximum TM value ($\mu\text{g}/\text{sample}$) and Time Attained	Maximum MBC value ($\mu\text{g}/\text{sample}$) and Time Attained	Minimum TM value $\mu\text{g}/\text{sample}$	Number of TM Samples > 1,000 $\mu\text{g}/\text{sample}$ ¹
Roses - after 2nd application	1,830 (DAT-1)	87.8 (DAT-21)	<LOQ (DAT-84)	13/ 27 total (36%)
Chrysanthemums - after 2nd application	2,510 (DAT 0)	164 (DAT-14)	79 (DAT-84)	24/ 36 total (67%)

Note: LOQ = 10 $\mu\text{g}/\text{sample}$

1. Highest field fortification level

MBC residues were above LOQ throughout the sampling period, slowly rising to a maximum 2 and 3 weeks after application for mums and roses, respectively. These data do not fit a first order dissipation pattern.

Elf Atochem performed a statistical analysis of the data as follows. Dissipation half-lives for thiophanate methyl DFR were calculated based on a linear regression of the natural logarithms of uncorrected, average DFR values at certain specific time-points. For TM residues on roses, the authors used DAT-1, 3, 5, 7, 14, and 21 data after the first application only. For TM residues on mums, the authors used DAT-0, 1, 3, 5, and 7 data after the first application only. This resulted in calculated thiophanate -methyl dissipation half-lives of 18.2 days on roses ($R^2=0.95$), and 18.7 days on mums ($R^2=0.91$). Dissipation half-lives for MBC were not calculated, since the magnitude of the MBC values was judged to be too low.

Versar re-ran the dissipation kinetics analysis using all individual data points (not averages) for DAT-0 through DAT-84 for both thiophanate methyl and MBC after the second application. Versar did not correct the DFR data. Versar then applied Microsoft EXCEL®'s 7.0 linear regression function to log (ln) transformed data. See Table 3, below, for a comparison between Elf Atochem and Versar-calculated residue half-lives.

Versar found that MBC residues, though low, were well above LOQ for many weeks after application, and were higher on mums than on roses. Versar agrees with Elf Atochem that these DFR data do not fit a first order dissipation paradigm. A linear regression run on the MBC on mums DFR data-set yielded a dissipation half-life of 44 days ($R^2 = 0.53$) and for roses, the dissipation half-life was 51 days ($R^2 = 0.20$).

Table 3. Thiophanate Methyl Half-lives as Estimated by Elf Atochem and Versar

Regression Method	Roses		Chrysanthemums	
	Half-life (days)	Correlation Coefficient (R^2)	Half-life (days)	Correlation Coefficient (R^2)
Calculated by Elf Atochem	18.2	0.95	18.7	0.91
Calculated by Versar	11.8	0.85	19.0	0.91

Data Variability

Versar examined data variability as part of Versar's linear regression exercise and found that coefficients of variance for replicate samples ranged as follows:

- Thiophanate methyl on roses: from 0.4 percent to 145 percent (the latter at DAT-84)
- Thiophanate methyl on mums: from 1.55 percent to 76.3 percent (the latter at DAT-84)
- MBC on roses: from 6.92 percent to 40.1 percent.
- MBC on mums: from 0.55 percent to 147 percent (the latter at DAT-84)
-

There are no specific requirements concerning the variability of replicate samples in the Pesticide Assessment Guidelines.

Compliance Checklist

Compliance with OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar Residue Dissipation: Agricultural, is critical. The itemized checklist below describes compliance with the major technical aspects of OPPTS 875.2100, and is based on the "Checklist for Residue Dissipation Data" used for study review by the U.S. EPA/OPP/HED.

- *Typical end use products of the active ingredient used.* This criterion was met.

- *Dislodgeable foliar residue (DFR) data to be collected from at least three geographically distinct locations for each formulation.* This criterion was not met. Instead, data were collected from two cut flower species at a single location.
- *The production of metabolites, breakdown products, or the presence of contaminants of concern, should be considered in the study design on a case-by-case basis.* This criterion was met. Samples were analyzed for MBC, a breakdown product of thiophanate-methyl.
- *Site(s) treated representative of reasonable worst-case climatic conditions expected in intended use areas.* This criterion is not relevant.
- *Applications occurred at time of season that the end-use product is normally applied to achieve intended pest control.* This criterion was met. Applications were made to mature plants.
- *End use product applied by application method recommended for the crop. Application rate given and should be at the least dilution and highest, label permitted, application rate.* These criteria were partially met. The application rate applied may not have been the maximum permitted. The rate used was ~16 oz formulated product per 100 gallons. The product label permits 24 oz formulated product per 100 gallons. Two applications were made, at a reapplication frequency which was shorter than that referenced on the label. The application methods used were acceptable.
- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was partially met. Two applications were made at each test site, at 7 day intervals. More applications are probably permitted by the label, since the label permits applications to be made “as needed” at a lower application rate.
- *A minimum of 400 cm² foliar material was collected per DFR sample.* This criterion was met.
- *Foliar residue data expressed as µg/cm² leaf surface area.* This criterion was satisfied.
- *Sampling should be sufficient to cover three half-lives and establish a dissipation curve. Recommended sampling intervals are 1 hour, 4 hours, 8 hours, 12 hours, 1, 2 and 3 days after application.* This criterion was probably met. Samples were collected up to DAT-84. Field DFR samples from roses were probably at or near LOQ by this time. Samples from chrysanthemums still contained significant residues by DAT-84.
- *Meteorological conditions including temperature, wind speed, daily rainfall, and humidity provided for the duration of the study.* This criterion was mostly met.

Greenhouse environmental conditions were controlled by a computer. Summary data on maximum and minimum temperature and humidity (daily average throughout sampling and application period) were provided.

- *Reported residue dissipation data in conjunction with toxicity data must be sufficient to support the determination of a reentry interval.* This criterion was partially met. No toxicity data was provided with this study report.
- *Residue storage stability, method efficiency (residue recovery), and limit of quantitation (LOQ) provided.* These criteria were partially met. Concurrent laboratory recovery and field fortification recovery values were provided in the report. Field fortification levels were not well chosen, since a high percentage of the field sample results were higher than the highest fortification level analyzed. There were also not enough field fortified sample replicates prepared at each round. The LOQ was 10 µg/sample. The LOD was not defined. How the authors defined the LOQ with respect to the LOD was not explained.
- *Duplicate foliar and/or soil samples collected at each sampling interval.* This criterion was partially satisfied. Triplicate field DFR samples were collected at each sampling interval. However, field fortified controls were analyzed in triplicate only on the first of five occasions. All the rest of these results are reported as single values.
- *Control and baseline foliar or soil samples collected.* The criterion was met. Control samples were collected from a control greenhouse at each sampling interval. Blank detergent solutions were also analyzed. No soil samples were collected.

Appendix A

Versar's Regression Analysis for Thiophanate Methyl Turf Transfer Residue Data

Raw Data

LOQ (in DFR Units): 0.025

DFR Units: ug/cm2

Trial 1

Name of Trial: TM on Roses

Output Sheet Name: TM on Roses

Days after Application	Residue Conc.
0	2.492842334
0	3.578833054
0	3.652877875
1	3.455425017
1	3.924375555
1	4.51673413
3	3.085200908
3	3.899693948
3	3.529469839
5	3.307335374
5	3.282653766
5	3.307335374
7	2.231217297
7	2.789021621
7	2.961792872
14	2.018955474
14	2.265771547
14	2.443479119
21	1.424128739
21	2.016487314
21	2.07078685
28	0.293711126
28	0.256688716
28	0.377628591
42	0.269029519
42	0.64418995
42	0.792279593
56	0.026162504
56	0.074044822
56	0.501036628
70	0.030605193
70	0.093790108
70	0.139697897
84	0.012340804
84	0.012340804
84	0.205350972

Trial 2

Name of Trial: TM on Mums

Output Sheet Name: TM on Mums

Days after Application	Residue Conc.
0	5.578043242
0	5.923585744
0	6.195083424
1	5.578043242
1	5.923585744
1	5.355908777
3	4.862276631
3	5.306545562
3	4.492052522
5	4.961003061
5	4.51673413
5	5.207819133
7	4.492052522
7	4.121828413
7	5.133774311
14	4.590778952
14	4.51673413
14	5.158455919
21	3.406061803
21	3.332016981
28	3.208608945
28	2.961792872
28	3.208608945
42	1.036627505
42	0.760193504
42	1.480896436
56	0.34060618
56	0.513377431
56	0.498568467
70	0.515845592
70	0.597294896
70	0.834238326
84	0.219666305
84	0.194984697
84	0.696021325

Raw Data

LOQ (in DFR Units): 0.025
 DFR Units: ug/cm2

Trial 3

Name of Trial: MBC on Roses
 Output Sheet Name: MBC on Roses

Trial 4

Name of Trial: MBC on Mums
 Output Sheet Name: MBC on Mums

Days after Application	Residue Conc.
0	0.039490572
0	0.054793168
0	0.039984204
1	0.063184915
1	0.075032086
1	0.082436568
3	0.080955672
3	0.105143647
3	0.098232797
5	0.103662751
5	0.104650015
5	0.103662751
7	0.107611808
7	0.116990818
7	0.124888933
14	0.147596011
14	0.159443183
14	0.176967124
21	0.15771547
21	0.203870076
21	0.216704512
28	0.057754961
28	0.048869582
28	0.060716754
42	0.038009675
42	0.15648139
42	0.144140586
56	0.012340804
56	0.012340804
56	0.099220061
70	0.012340804
70	0.0691085
70	0.073057558
84	0.012340804
84	0.012340804
84	0.221640833

Days after Application	Residue Conc.
0	0.148089644
0	0.207325501
0	0.182643894
1	0.162898608
1	0.212261822
1	0.177707572
3	0.256688716
3	0.27149768
3	0.241879751
5	0.246816073
5	0.256688716
5	0.291242966
7	0.251752394
7	0.232007108
7	0.281370323
14	0.404778359
14	0.33813802
14	0.293711126
21	0.249284233
21	0.320860894
28	0.308520091
28	0.266561358
28	0.325797216
42	0.148089644
42	0.099220061
42	0.151791885
56	0.04714187
56	0.077253431
56	0.066887156
70	0.103415934
70	0.103169118
70	0.18980156
84	0.062691282
84	0.030852009
84	0.124888933

Regression Analysis: Summary Output for MBC on Mums
MRID 450275-01

<i>Regression Statistics</i>	
Multiple R	0.731519
R Square	0.53512
Adjusted R ²	0.521033
Standard Error	0.423223
Observations	35

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Signif. F</i>
Regression	1	6.80398	6.80398	37.986084	5.9714E-07
Residual	33	5.910884	0.179118		
Total	34	12.71486			

		<i>Coeff.</i>	<i>Std. Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	-	1.30078	0.100569	-12.9342	1.795E-14	-1.505389555	-1.096169777
Slope	-	0.01569	0.002545	-6.16329	5.971E-07	-0.020865725	-0.010508883

Half Life = 44.18523Days

MBC on Mums

Predicted DFR Levels

Time (Days)	Residue (ug/cm2)	Time (Days)	Residue (ug/cm2)
0	0.272319	21	0.1958878
1	0.268081	22	0.1928389
2	0.263908	23	0.1898373
3	0.2598	24	0.1868825
4	0.255757	25	0.1839737
5	0.251776	26	0.1811102
6	0.247857	27	0.1782912
7	0.243999	28	0.1755162
8	0.240201	29	0.1727843
9	0.236463	30	0.1700949
10	0.232782	31	0.1674474
11	0.229159	32	0.1648411
12	0.225592	33	0.1622754
13	0.222081	34	0.1597496
14	0.218624	35	0.1572631
15	0.215221		
16	0.211871		
17	0.208573		
18	0.205327		
19	0.202131		
20	0.198985		

Regression Analysis: Means and CVs for MBC on Mums

Days after Last Treatment	Residues (ug/cm2)	Mean (ug/cm2)	Standard Deviation (ug/cm2)	Coefficient of Variation (%)
0	0.14809	0.179	0.0298	16.6
	0.207326			
	0.182644			
1	0.162899	0.184	0.0253	13.8
	0.212262			
	0.177708			
3	0.256689	0.257	0.0148	5.76
	0.271498			
	0.24188			
5	0.246816	0.265	0.0233	8.8
	0.256689			
	0.291243			
7	0.251752	0.255	0.0248	9.74
	0.232007			
	0.28137			
14	0.404778	0.346	0.0559	16.2
	0.338138			
	0.293711			
21	0.249284	0.285	0.0506	17.8
	0.320861			
28	0.30852	0.3	0.0305	10.2
	0.266561			
	0.325797			
42	0.14809	0.133	0.0293	22.1
	0.09922			
	0.151792			
56	0.047142	0.0638	0.0153	24
	0.077253			
	0.066887			
70	0.103416	0.132	0.0499	37.8
	0.103169			
	0.189802			
84	0.062691	0.0728	0.0478	65.7
	0.030852			
	0.124889			

Regression Analysis: Summary Output for MBC on Roses
MRID 450275-01

<i>Regression Statistics</i>	
Multiple R	0.448441
R Square	0.2011
Adjusted R ²	0.177603
Standard Error	0.776937
Observations	36

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Signif. F</i>
Regression	1	5.166171	5.166171	8.558497	0.006087146
Residual	34	20.52344	0.603631		
Total	35	25.68961			

		<i>Coeff.</i>	<i>Std. Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	-	2.25646	0.182625	-12.3557	3.991E-14	-2.627603064	-1.8853264
Slope	-	0.01366	0.004669	-2.92549	0.0060871	-0.023146526	-0.004170369

Half Life = 50.74861Days

MBC on Roses: Predicted DFR Levels

Time (Days)	Residue (ug/cm2)	Time (Days)	Residue (ug/cm2)
0	0.10472	21	0.0786072
1	0.103299	22	0.0775408
2	0.101898	23	0.0764889
3	0.100516	24	0.0754513
4	0.099152	25	0.0744278
5	0.097807	26	0.0734181
6	0.09648	27	0.0724222
7	0.095172	28	0.0714397
8	0.093881	29	0.0704706
9	0.092607	30	0.0695146
10	0.091351	31	0.0685716
11	0.090111	32	0.0676414
12	0.088889	33	0.0667238
13	0.087683	34	0.0658187
14	0.086494	35	0.0649258
15	0.08532		
16	0.084163		
17	0.083021		
18	0.081895		
19	0.080784		
20	0.079688		

Regression Analysis: Means and CVs for MBC on Roses

Days after Last Treatment	Residues (ug/cm ²)	Mean (ug/cm ²)	Standard Deviation (ug/cm ²)	Coefficient of Variation (%)
0	0.039491	0.0448	0.0087	19.4
	0.054793			
	0.039984			
1	0.063185	0.0736	0.00971	13.2
	0.075032			
	0.082437			
3	0.080956	0.0948	0.0125	13.1
	0.105144			
	0.098233			
5	0.103663	0.104	0.00057	0.548
	0.10465			
	0.103663			
7	0.107612	0.116	0.00865	7.46
	0.116991			
	0.124889			
14	0.147596	0.161	0.0148	9.18
	0.159443			
	0.176967			
21	0.157715	0.193	0.031	16.1
	0.20387			
	0.216705			
28	0.057755	0.0558	0.00617	11
	0.04887			
	0.060717			
42	0.03801	0.113	0.0651	57.6
	0.156481			
	0.144141			
56	0.012341	0.0413	0.0502	121
	0.012341			
	0.09922			
70	0.012341	0.0515	0.034	66
	0.069109			
	0.073058			
84	0.012341	0.0821	0.121	147
	0.012341			
	0.221641			

Regression Analysis: Summary Output for Thiophanate Methyl on Mums
MRID 450275-01

<i>Regression Statistics</i>	
Multiple R	0.953961
R Square	0.910042
Adjusted R ²	0.907316
Standard Error	0.332003
Observations	35

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Signif. F</i>
Regression	1	36.79733	36.79733	333.83631	7.94934E-19
Residual	33	3.637447	0.110226		
Total	34	40.43478			

	<i>Coeff.</i>	<i>Std. Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	1.811052	0.078893	22.95586	7.287E-22	1.650543546	1.971561056
Slope	-	0.001997	-18.2712	7.949E-19	-0.040543965	-0.032419413
	0.03648					

Half Life = 18.99987Days

TM on Mums

Predicted DFR Levels

Time (Days)	Residue (ug/cm2)	Time (Days)	Residue (ug/cm2)
0	6.116881	21	2.8432189
1	5.897748	22	2.7413627
2	5.686466	23	2.6431555
3	5.482752	24	2.5484664
4	5.286337	25	2.4571695
5	5.096958	26	2.3691432
6	4.914363	27	2.2842704
7	4.73831	28	2.2024382
8	4.568563	29	2.1235375
9	4.404898	30	2.0474633
10	4.247096	31	1.9741145
11	4.094947	32	1.9033933
12	3.948248	33	1.8352057
13	3.806805	34	1.7694608
14	3.670429	35	1.7060712
15	3.538939		
16	3.412159		
17	3.289921		
18	3.172062		
19	3.058425		
20	2.94886		

TM on Mums

Regression Analysis: Means and CVs for TM on Mums

Days after Last Treatment	Residues (ug/cm2)	Mean (ug/cm2)	Standard Deviation (ug/cm2)	Coefficient of Variation (%)
0	5.578043	5.9	0.309	5.24
	5.923586			
	6.195083			
1	5.578043	5.62	0.286	5.09
	5.923586			
	5.355909			
3	4.862277	4.89	0.408	8.34
	5.306546			
	4.492053			
5	4.961003	4.9	0.35	7.15
	4.516734			
	5.207819			
7	4.492053	4.58	0.512	11.2
	4.121828			
	5.133774			
14	4.590779	4.76	0.351	7.38
	4.516734			
	5.158456			
21	3.406062	3.37	0.0524	1.55
	3.332017			
28	3.208609	3.13	0.142	4.55
	2.961793			
	3.208609			
42	1.036628	1.09	0.364	33.4
	0.760194			
	1.480896			
56	0.340606	0.451	0.0958	21.2
	0.513377			
	0.498568			
70	0.515846	0.649	0.165	25.5
	0.597295			
	0.834238			
84	0.219666	0.37	0.282	76.3
	0.194985			
	0.696021			

Regression Analysis: Summary Output for Thiophanate Methyl on Roses
MRID 450275-01

<i>Regression Statistics</i>	
Multiple R	0.922812
R Square	0.851583
Adjusted R ²	0.847217
Standard Error	0.700092
Observations	36

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Signif. F</i>
Regression	1	95.61614	95.61614	195.08353	1.2052E-15
Residual	34	16.66439	0.490129		
Total	35	112.2805			

	<i>Coeff.</i>	<i>Std. Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	1.380883	0.164562	8.391261	8.496E-10	1.046453205	1.71531357
Slope	-	0.004207	-13.9672	1.205E-15	-0.067309746	-0.050210462
	0.05876					

Half Life = 11.79622Days

TM on Roses

Predicted DFR Levels

Time (Days)	Residue (ug/cm2)	Time (Days)	Residue (ug/cm2)
0	3.978415	21	1.1582627
1	3.751378	22	1.092164
2	3.537298	23	1.0298375
3	3.335435	24	0.9710677
4	3.145091	25	0.9156517
5	2.96561	26	0.8633982
6	2.796372	27	0.8141266
7	2.636791	28	0.7676668
8	2.486317	29	0.7238583
9	2.34443	30	0.6825498
10	2.210641	31	0.6435987
11	2.084486	32	0.6068704
12	1.96553	33	0.5722381
13	1.853363	34	0.5395822
14	1.747597	35	0.5087898
15	1.647867		
16	1.553828		
17	1.465156		
18	1.381544		
19	1.302703		
20	1.228362		

Regression Analysis: Means and CVs for TM on Roses

Days after Last Treatment	Residues (ug/cm2)	Mean (ug/cm2)	Standard Deviation (ug/cm2)	Coefficient of Variation (%)
0	2.492842	3.24	0.649	20
	3.578833			
	3.652878			
1	3.455425	3.97	0.532	13.4
	3.924376			
	4.516734			
3	3.085201	3.5	0.408	11.7
	3.899694			
	3.52947			
5	3.307335	3.3	0.0142	0.432
	3.282654			
	3.307335			
7	2.231217	2.66	0.382	14.4
	2.789022			
	2.961793			
14	2.018955	2.24	0.213	9.52
	2.265772			
	2.443479			
21	1.424129	1.84	0.359	19.5
	2.016487			
	2.070787			
28	0.293711	0.309	0.062	20.1
	0.256689			
	0.377629			
42	0.26903	0.568	0.27	47.5
	0.64419			
	0.79228			
56	0.026163	0.2	0.261	131
	0.074045			
	0.501037			
70	0.030605	0.088	0.0548	62.2
	0.09379			
	0.139698			
84	0.012341	0.0767	0.111	145
	0.012341			
	0.205351			



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Chemical: Thiophanate-methyl

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